Adsorption of Pb(II) Ions Using Residual Extract of Alginate from *Sargassum sp*.

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Abstract

Lead ion is one of the environment's main pollutants. Lead ions have carcinogenic and toxic effects and, therefore dangerous to the human body. This research was conducted to determine the ability of alginate extraction residue from *Sargassum sp*.'s ability as lead ion adsorbent. The characterization of this adsorbent was done using FTIR (*Fourier Transform Infrared*) and SEM-EDS (*Scanning Electron Microscopy-Energy Dispersive Spectroscopy*). The optimization of this adsorbent was carried out toward some parameters, such as pH, adsorbent's mass, Pb(II)'s initial concentration, and contact time. The result showed that the optimum condition can be reached if the contact between the adsorbent and adsorbate was done using 0,025 grams of adsorbent in 25 ml of pH 5 Pb(II) (200 ppm) solution, using 5 minutes contact time. The adsorption process follows the Langmuir isotherm model with a maximum capacity of 416,6667 mg.g^{-1}. The result of the kinetics study showed that the adsorption follows a pseudo-second-order kinetics whilst the thermodynamics study showed that the adsorption process is exothermic with the value of ΔH^o = -4,51 kJ.mol^{-1}, and the value of ΔS^o = -0,038 kJ.mol^{-1}.K^{-1}.

Keywords: *Lead, adsorption, adsorbent, residue, extraction, seaweed.*

Abstrak

Ion timbal merupakan salah satu pencemar yang umum ditemukan di lingkungan. Ion timbal memiliki efek karsinogenik dan toksik sehingga berbahaya bagi manusia. Penelitian ini bertujuan untuk mempelajari kemampuan residu dari ekstraksi alginat dari *Sargassum sp* sebagai adsorben ion timbal. Karakterisasi adsorben dilakukan menggunakan FTIR (*Fourier Transform Infrared*) dan SEM-EDS (*Scanning Electron Microscopy-Energy Dispersive Spectroscopy*). Parameter yang dioptimasi adalah pH larutan, massa adsorben, konsentrasi awal ion Pb(II), dan waktu kontak. Hasil eksperimen menunjukkan bahwa kondisi optimum dicapai saat pH larutan 5, massa adsorben 0,025 gram, konsentrasi awal ion Pb(II) 200 ppm dan waktu kontak 5 menit. Proses adsorpsi mengikuti model isoterm Langmuir dengan kapasitas maksimum 416,67 mg.g^{-1}. Hasil studi kinetika menunjukkan adsorpsi mengikuti kinetika reaksi orde dua semu. Adsorpsi ion Pb (II) berlangsung secara eksotermik dengan nilai ΔH^o = -4,51 kJ.mol^{-1}, dan nilai ΔS^o = -0,038 kJ.mol^{-1}.K^{-1}.

Kata Kunci: *Timbal, adsorpsi, adsorben, residu, ekstraksi, rumput laut.*

1. Introduction

Heavy metal pollution is an issue that we cannot ignore because heavy metal pollution is a hazard to the body and the environment. Heavy metal pollution can occur due to industrial waste, mining, volcanic activity, and coastal abrasion. Heavy metals are metals that have a density exceeding 5000 kg/m^3. Some types of heavy metals are aluminum, mercury, lead, zinc, chromium, and cadmium.

Lead is a metal that can pollute water, soil, plants, and animals, and is toxic if swallowed or inhaled, because lead can affect almost all organs in the human body, is carcinogenic, can cause mutations, decomposes over a long period and its toxicity does not change [1]. Lead can enter the body through food, be absorbed into the blood, inhibit the work of enzymes, and replace other metals as cofactors in enzymatic reactions. The specific impact of lead is causing nervous system disorders, intestinal disorders, kidney damage, reproductive system disorders, and disruption of blood formation.

There are several methods to remove metals from water, for example by adsorption, filtration, precipitation, ion exchange, membrane technology, and biosorption. Biosorption is the process of adsorption of metal ions that utilizes biological materials and is based on plant biomass or animal polymers. The most widely used biosorption is biosorption from algae because algae are widely found in nature [2].

Seaweed polysaccharides have received much attention from industry and researchers to develop the industry globally. Important seaweed polysaccharides are alginate, agarose, and carrageenan [3, 4, 5], which are commonly used in the preparation of food products [6]. Alginate is a salt of branched copolymer, with 14 linkages of β-D-mannuronic acid and α-L-guluronic acid anionic polymers that are commonly isolated from brown seaweeds. Alginate is widely used to maintain the structure of frozen foods [4], salad dressings [7], tableting agents [8], matrix for immobilized systems [9,10] matrices, dental impression materials [11, 12], tissue engineering [13, 14, 15], and drug delivery systems [16, 17]. In the alginate extraction process, the residue is usually discarded or used for animal feed. After alginate extraction, the residue still contains many constituents of raw seaweed, so it has the potential for heavy metal adsorption because its content is carboxyl alginate, phosphate, and amino and hydroxy groups [18]. In this study, the residue from alginate extract is expected to be able to adsorb heavy metal Pb^{2+} in solution.

2. Material and Metods

Material

The materials used in this research are *Sargassum sp.* seaweed (taken from the waters of Dompu, NTB), formaldehyde, Na_2CO_3, HCl, HNO_3, $Pb(NO_3)_2$, and aqua dm. SEM-EDS characterization was conducted in the Geology building of ITB, and coating for SEM-EDS was conducted in the CAS (*Center of Advance Science*) building of ITB.

Preparing of Sargassum sp. Seaweed Residue.

Firstly, the *Sargassum sp.* seaweed was washed and then dried in the oven for 24 hours at 60°C. Then seaweed was blended and filtered with a 160 *mesh* sieve. Then 15 grams of seaweed soaked in formaldehyde solution (CHOH: 0.4% w/w) 250 mL for 30 minutes. After that, the seaweed was rinsed and soaked using 0.1 M hydrochloric acid (HCl) solution 150 mL for 2 hours. Next, the seaweed was put into a solution of Na_2CO_3 (2% w/v) while heated to 60ºC for 5 hours. After that, the solution was filtered and the solids were taken (extraction residue). The residue was then protonated by adding HCl with constant stirring until it reached pH 5 (*biomass* concentration 10 g/L). Adsorbent candidates were selected by making adsorbent variations with the original shape, with protonation times of 3 hours, 6, hours, and 9 hours, then variations were also made using HCl concentrations of 0.01 M, 0.1M, and 1 M. The biomass was then rinsed with distilled water and washed with water. The *biomass* was then rinsed with distilled water and dried in an oven at 60°C.

Characterization and analysis

The adsorbent was characterized using FTIR (*Fourier Transform Infrared Spectroscopy*) to determine its functional groups and SEM-EDS (*Scanning Electron Microscope - Energy Dispersive Spectroscopy)* to determine its morphology and elemental composition.

Determination of Optimum pH of Pb(II) Ion Adsorption

$Pb(NO_3)_2$ solution of 100 mg.L^{-1} pH 1, 2, 3, 4, and 5 was prepared by adding HNO_3 solution to the desired pH condition. Then, 25 mL of $Pb(NO_3)_2$ solution was contacted with 0.1 g adsorbent in a closed erlenmeyer, stirred at 200 rpm using a shaker for 1 hour, and the lead content using AAS (Atomic Absorption Spectroscopy).

Determination of Optimum Seaweed Residue Adsorbent Mass for Pb(II) Ion Adsorption

A total of 25 mL of 100 mg.L^{-1} $Pb(NO_3)_2$ solution was contacted with adsorbents of different masses (0.025; 0.05; 0.07; 0.1; 0.15; and 0.2 grams) in a closed erlenmeyer, and stirred at 200 rpm using a shaker for 1 hour. Then the solution was filtered and measured for lead content using AAS.

Determination of Equilibrium Time of Seaweed Residue Adsorbent for Pb(II) Ion Adsorption

A total of 25 mL of 100 mg.L^{-1} $Pb(NO_3)_2$ solution was contacted with adsorbent with a mass of 0.0250 grams in a closed erlenmeyer and stirred at 200 rpm using a shaker for various times (1; 3; 5; 7; 9; 15; 30; 45; 60; 75; 100; 120; 160; 180; and 240 minutes). Then the solution was filtered and measured for lead content using AAS.

Determination of Initial Concentration of Pb (II) Metal Ion Solution

A total of 25 mL of $Pb(NO_3)_2$ solution with various concentrations (100; 200; 300; 400; 500; and 600 $mg.L^{-1}$) was contacted with adsorbent with a mass of 0.0250 grams in a closed erlenmeyer, and stirred at 200 rpm using a shaker for 5 minutes. Then the solution was filtered and measured for lead content using AAS.

Adsorption Isotherm and Thermodynamic Study

A total of 25 mL of $Pb(NO_3)_2$ solution with varying concentrations (100; 200; 300; 400; 500; and 600 $mg.L^{-1}$) was contacted with adsorbent with a mass of 0.0250 grams in an erlenmeyer with a lid, and stirred at 200 rpm using an incubator shaker at room temperature, temperature 40°C, and temperature 55°C for 5 minutes. Then the solution was filtered and measured for lead content using AAS.

Desorption Process

A total of 25 mL of $Pb(NO_3)_2$ pH 3 solution with a concentration of 200 ppm was contacted with adsorbent with a mass of 0.0250 grams in a closed erlenmeyer, and stirred at 200 rpm for 5 minutes. Then the solution was filtered and measured for lead content using AAS. Then the same adsorbent was put into 25 ml of 0.01; 0.1; and 0.5 M HNO_3 solution in a 100 ml capped erlenmeyer and stirred at 200 rpm for 5 minutes to perform the desorption process. Then the solution was filtered and for lead content using AAS.

Repeated Adsorption Process

A total of 25 mL of $Pb(NO_3)_2$ pH 3 solution with a concentration of 200 ppm was contacted with adsorbent with a mass of 0.0250 grams in a closed erlenmeyer, and stirred at 200 rpm for 5 minutes. Then the solution was filtered and the lead content was measured using AAS. The same adsorbent was then placed into a fresh 200 ppm $Pb(NO_3)_2$ pH 3 solution in a sealed erlenmeyer flask and stirred at 200 rpm for 5 minutes to re-adsorb. The solution was then filtered and the lead content was measured using AAS. This process was carried out continuously until each adsorbent adsorbed 10 pieces of $Pb(NO_3)_2$ pH 3 solution with different concentrations of 200 ppm.

3. Result and Discussion

*3.1 Preparation of Adsorbent from Extraction Residue of Sargassum sp. Seaweed.*

In this study, the seaweed used from the genus *Sargassum*, which comes from the waters of Dompu Regency, NTB. Brown seaweed was chosen because seaweed is a potential source. After all, alginate is the main component of seaweed cell walls and can reach 40% of the dry weight of algae so it contains 70% binding sites [19].

The extraction process is carried out by adding Na_2CO_3 solution at a temperature of 60°C because Na_2CO_3 can help the process of expansion (swelling) of the tissue of algae cells, thus facilitating the release of alginate from algae tissue. After that, filtering separates the Na-alginate dissolved in the filtrate from the residue in the form of solids. Then the solids were oven dried at 60°C to obtain seaweed residue adsorbent granules as shown in **Figure 1**.


Figure 1. Photo of adsorbent

In the selection of adsorbent candidates, variations in protonation time and protonation concentration were performed. The following are the results.
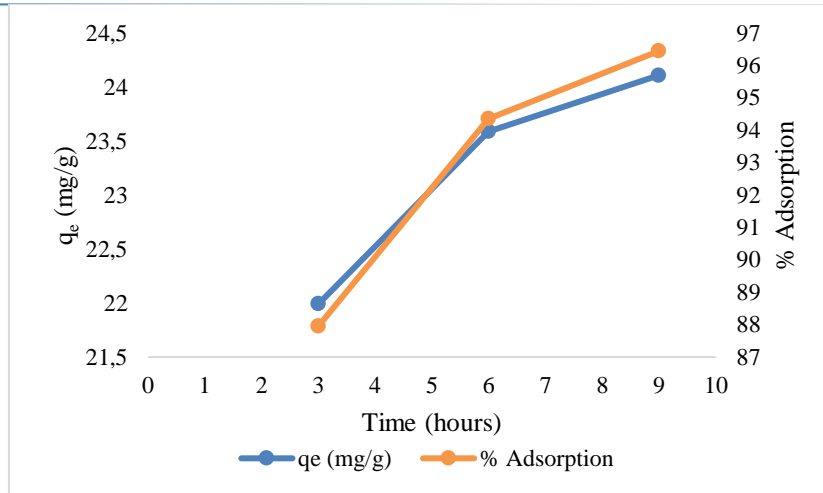
Figure 2. Determination of Protonation Time.

From the results of the protonation time variation as shown in **Figure 2**, the results tended to be flat, so by considering the effectiveness, the optimum time was taken at the protonation time of 6 hours.
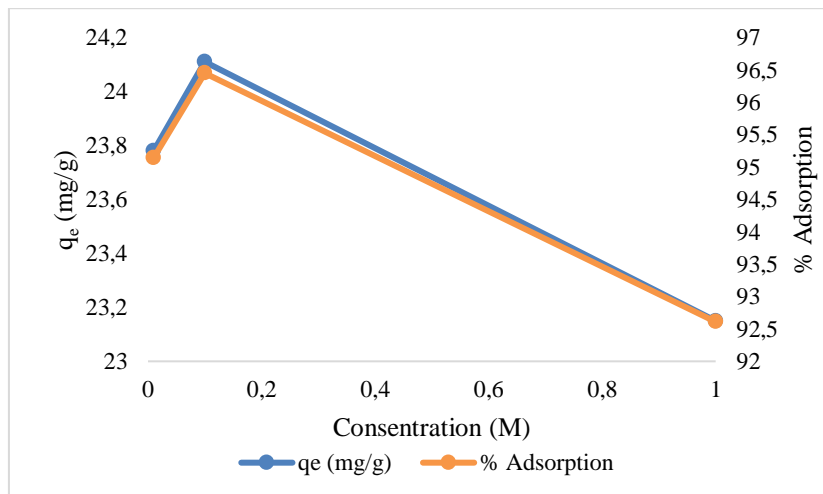
Figure 3. Determination of HCl concentration

In the concentration variation as shown in **Figure 3**, an insignificant difference was also obtained, but there was a peak at 0.01 M protonation, so the results with 0.01 M protonation were used.

3.2 Characterization of Seaweed Residue Adsorbent

Analysis using FTIR (*Fourier Transform Infrared*) Spectrophotometer to determine which groups play a role in the adsorption process on the residue before and after contact. The FTIR spectrum of Sodium alginate after being extracted from seaweed and seaweed residue is shown in **Figure 4**.
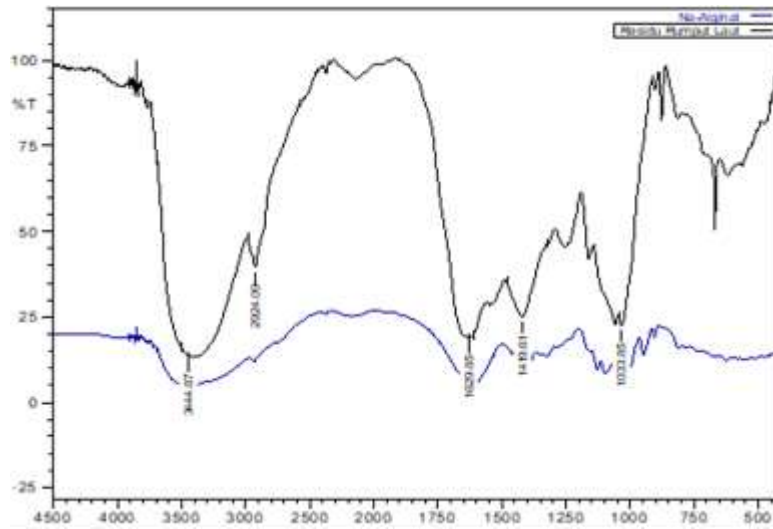
Figure 4. IR spectrum of seaweed residue and Na-alginate extract
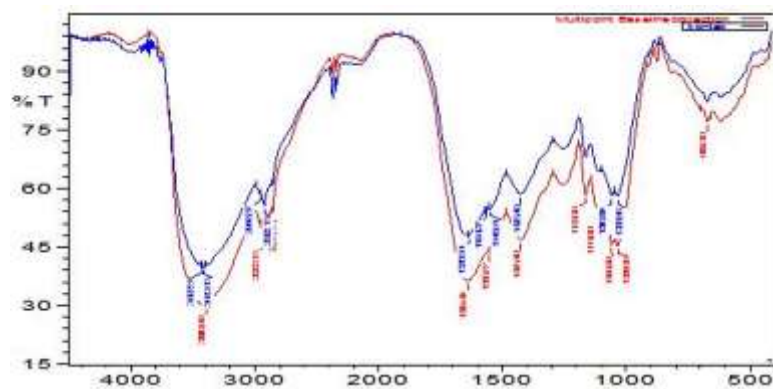

Figure 5. IR spectrum of seaweed residue adsorbent before and after contact

The IR spectrum of the seaweed residue adsorbent before and after contact is shown in **Figure 5.** The spectrum of Na-alginate (blue spectrum) and residue (black spectrum) obtained after extraction from seaweed has a peak at wave number 3400 cm^{-1} indicating the presence of -OH group, 1400 cm^{-1} indicating the presence of C-H group; 1050 cm^{-1} indicating the presence of C–O group in ether; 1650 cm^{-1} indicating C=O group in carboxylate and at wave number 2900 cm^{-1} indicating N–H group derived from protein [12]. From the two spectra, there is no significant change in the spectrum peak. So it can be said that the alginate extraction process was successful.

Table 1. Wave number change

Functional Group	Peak (before)	Peak (after)
C=O	1550,77	1564,27
C=O	1639,49	1635,64
O-H	3410,15	3427,51

In **Table 1,** the changes in functional groups are observed. In this spectrum, the blue line shows the spectrum of the adsorbent after contact and the red line shows the adsorbent before contact. In the IR spectrum, it was found that there was a change in wave numbers at wave numbers 1550, 1639, and 3410 cm^{-1}, so it can be concluded that the functional groups that influence this adsorption process are the C=O group in the carboxylate and the OH group.

Further characterization was carried out by testing with an SEM-EDS tool which functions to determine the morphology of the adsorbent surface before and after contact with Pb(II) ions. Based on

Figure 6 the morphology of the adsorbent before contact (a) has larger pores than the adsorbent after contact (b), which has smaller pores.

(a)   (b)
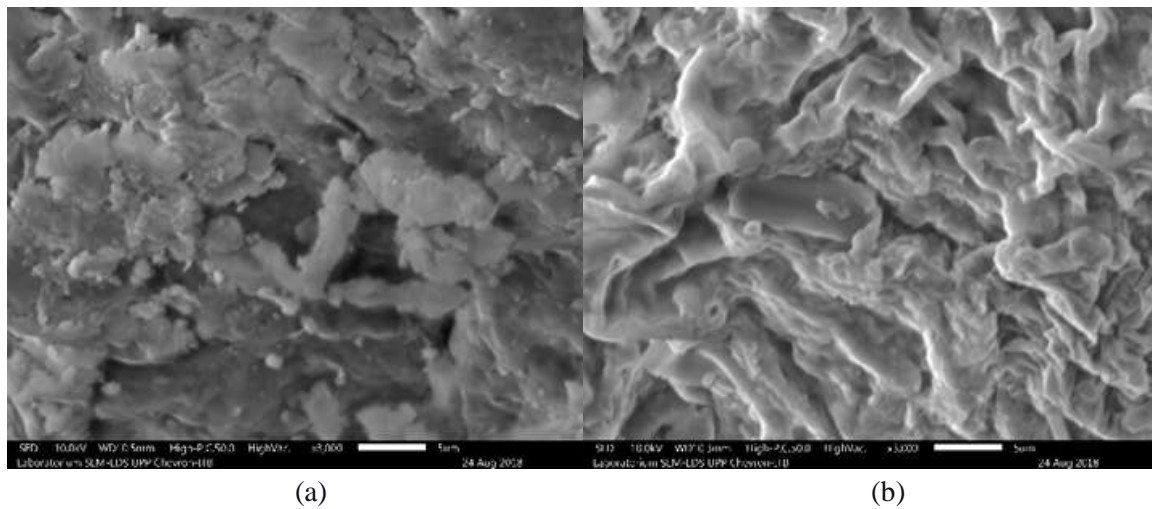
Figure 6. SEM image of Seaweed Residue adsorbent before being contacted with Pb(II) ions (a) and Seaweed Residue after being contacted with Pb(II) ions (b)

Table 2. EDS data of seaweed residue adsorbent before and after contact with Pb(II) ions

Element	% Mass	
	Before	After
C	52,47	38,7
O	24,92	32,59
Na	1,33	0,44
Mg	1,1	1,65
Al	1,34	2
Si	2,54	4,2
S	2,21	3,55
Ca	11,29	9,5
Pb	2,6	7,3

Measurement of the composition on the surface of the adsorbent was measured using EDS which is shown in **Table 2.** It was found that after contact the mass% of Pb increased and the mass % of Na and Ca decreased, so it can be concluded that the ion exchange that occurred was from Na and Ca with Pb.

3.3 Determination of pH for Pb(II) Ion Adsorption

The pH value is influential because it can protonate and deprotonate functional groups on the adsorbent. The optimization results can be seen in **Figure 7.**
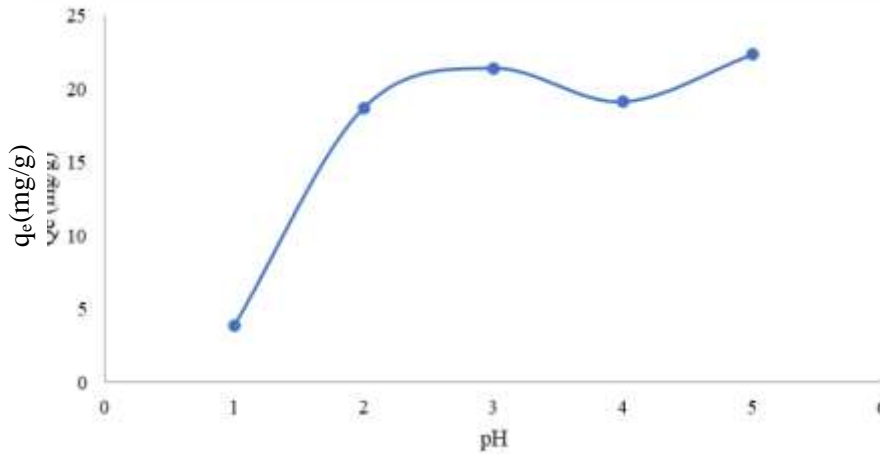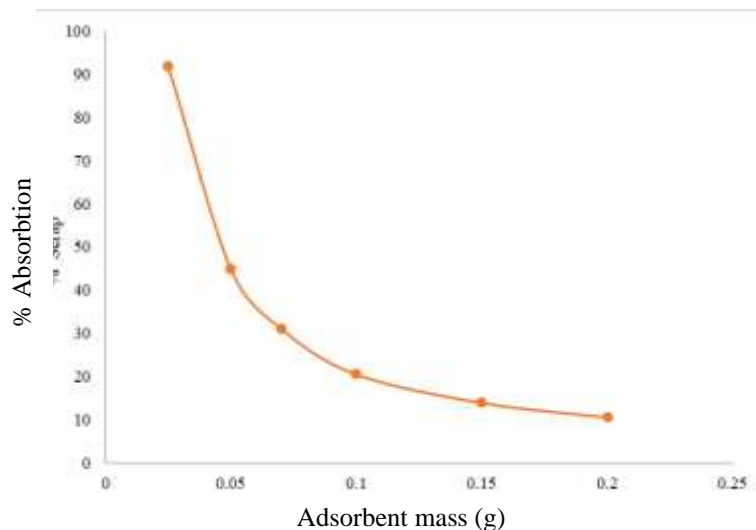
Figure 7. Determination of Pb(II) ion adsorption by seaweed residue adsorbent with pH variation 1-5

Figure 7 shows that at pH 1-2, there is an increase in absorption capacity at pH 3-5 began to fall this is because the number of H $^+$ ions is reduced so that the absorption capacity becomes quite stable, but from the optimization results obtained the optimum pH value is obtained at pH 5.

3.4 Determination of Adsorbent Mass of Seaweed Residue for Pb(II) Ion Adsorption
In determining the adsorbent mass, which was varied from a mass of 0.025; 0.05; 0.07; 0.1; 0.15; and 0.2, the experimental results were obtained as shown in **Figure 8.**
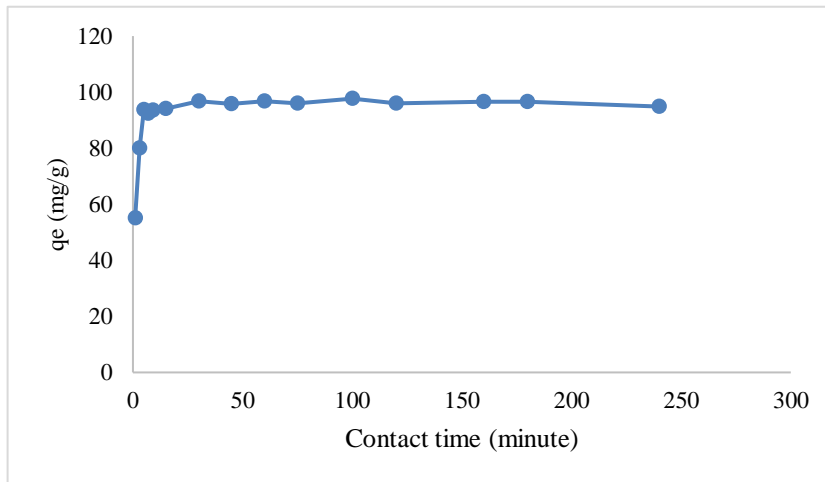

Figure 8. Determination of Pb(II) ion adsorption by adsorbent with adsorbent mass variation

Based on **Figure 8** above, it can be seen that the increase in adsorbent mass decreases the percent uptake of Pb(II) ions. The adsorption capacity of the adsorbent decreases as the number of adsorbents increases due to the fixed concentration of Pb(II) ions in the solution. From the experiment, the optimum uptake of Pb(II) ions was obtained at a mass of 0.025 grams.

3.5 Determination of Time to Reach Equilibrium of Seaweed Residue Adsorbent for Adsorption of Pb(II) Ion
Contact time variations were made at 1 minute to 240 minutes. The experimental results are shown in **Figure 9.**
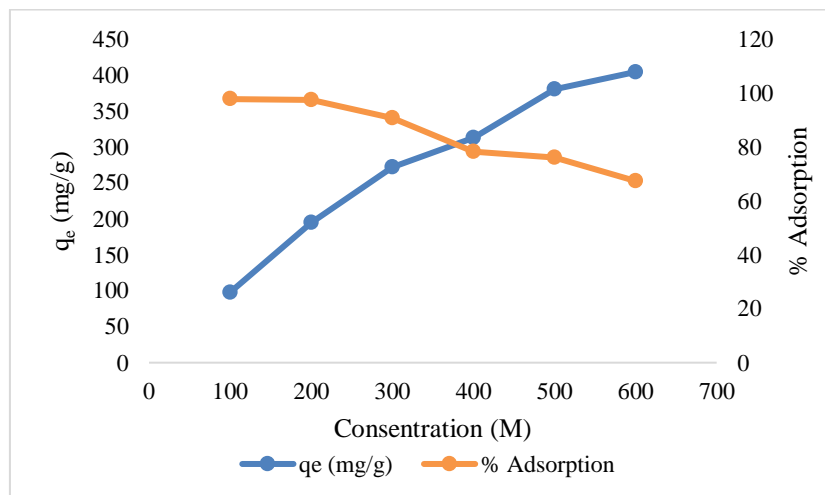
Figure 9. Determination of adsorption of Pb(II) ions by seaweed residue adsorbent with the variation of contact time.

Based on the results, it was found that when the adsorption process was carried out at 1 minute and 3 minutes, the percent adsorption of the adsorbent still tended to be small. After 5 minutes the percent adsorption of the adsorbent has exceeded 90%, and after varying up to 240 minutes, there is no significant change, so it can be concluded that the equilibrium time has been reached at 5 minutes.

3.6 Determination of Initial Concentration of Pb(II) Ion Solution

Based on **Figure 10**, it is known that as the concentration of Pb(II) ions in solution increases, the adsorbent experiences an increase in adsorption capacity and a decrease in the percent uptake of Pb(II) ions. From the results, it was found that at a concentration of 300 ppm the adsorbent was saturated. The optimum concentration was achieved when the Pb(II) solution used had a concentration of 200 ppm.

Figure 10. Determination of initial concentration of Pb(II) ions by seaweed adsorbent

3.7 Isotherm Study

Adsorption isotherms were conducted to determine the interactions between the seaweed residue adsorbent and the Pb(II) ion adsorbate. Two types of isotherms were studied namely the Langmuir and Freundlich isotherms. Based on **Figure 11**, it is known that the adsorption process of Pb(II) ions by the seaweed residue adsorbent follows the Langmuir isotherm model, as evidenced by a more appropriate fitting curve and the R^2 value.
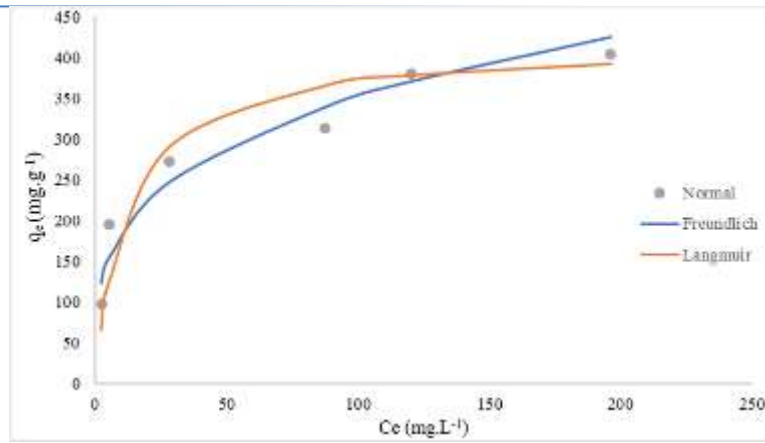
Figure 11. Langmuir isotherm and Freundlich isotherm model curves

Table 3. Parameters of Langmuir adsorption isotherm and Freundlich adsorption isotherm

Isotherm parameters	T (K)		
	300	313	328
Langmuir Isotherm			
K_L	0,0814	0,0444	0,0426
q_{max} (mg.g^{-1})	416,6667	500	500
R^2	0,9869	0,9783	0,9668
Freundlich Isotherm			
K_F	96,8724	69,9037	62,0012
n	3,5676	2,6674	2,4956
R_F^2	0,9087	0,8681	0,8836

Based on **Table 3**, the q_m value of this experiment is close to the maximum q_e value, which is 404.00 mg.g^{-1}, this shows that the adsorption process of Pb(II) ions follows the Langmuir isotherm model. The adsorption process by following the Langmuir isotherm model assumes that the adsorption process takes place homogeneously and the adsorbed Pb(II) ions only form one layer (monolayer). In the Freundlich isotherm, the resulting n>1 value shows that the interaction strength increases.

3.8 Adsorption Kinetics

The studied kinetic model of Pb(II) ion adsorption is modeled with pseudo-first-order and pseudo-second-order equations. Based on **Figure 12**, it was found that the Pb(II) ion adsorption process follows pseudo-second-order reaction kinetics with R^2 value = 0.9998. Pseudo-second order kinetics assumes that the rate of the adsorption process is influenced by two different factors.
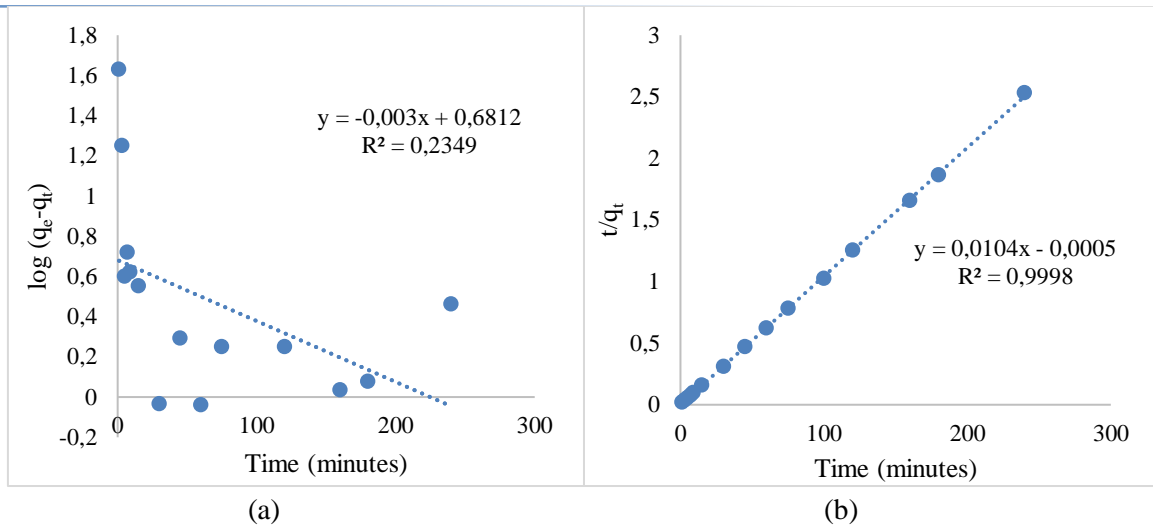
Figure 12. Adsorption kinetics model (a) Pseudo-first-order (PFO) and (b) Pseudo-second-order

Table 4. Kinetic parameters of Pb(II) ion adsorption by seaweed residue adsorbent

c $(mg.g^{-1})$	Pseudo-first-order			Pseudo-second-order		
	Qe $(mg.g^{-1})$	k_1 (min^{-1})	R^2	Qe $(mg.g^{-1})$	k_2 $(mg.L^{-1}.min^{-1})$	R^2
97,6834	4,63340219	0,00737	0,2439	96,1538462	0,21632	0,9998

Based on **Table 4**, the experimental pseudo-second-order kinetics qe value is close to the experimental q_e value, so it can be concluded that the adsorption kinetics of Pb(II) ions with seaweed residue adsorbent follow pseudo-second-order kinetics.

3.9 Thermodynamic Study

The study of thermodynamics was used to study the thermodynamics of adsorption of Pb(II) ions by seaweed residue adsorbent. To determine the values of thermodynamic parameters, the concentration of Pb(II) ions was varied at various temperatures. The value of thermodynamic parameters obtained by plotting the value of 1/T against KL is shown in **Figure 13.**
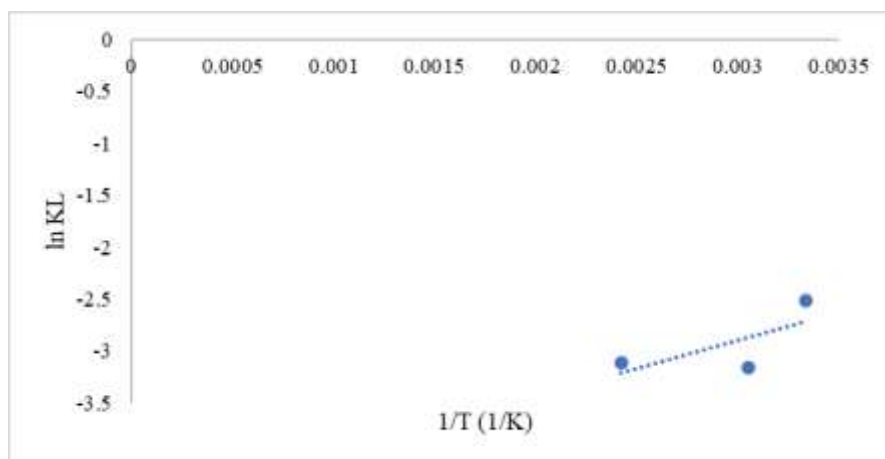

Figure 13. Alignment of 1/T value against K_L

Based on the curve in **Figure 13**, the values of free energy change ($^{\Delta Go}$), enthalpy change ($^{\Delta Ho}$), and entropy change ($^{\Delta So}$) can be obtained as shown in **Table 5**.

$$lnK_c = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT}$$

Table 5. Thermodynamic parameters of Pb(II) ion adsorption by seaweed residue adsorbent

T(K)	300	313	328
K_L (L.mg^{-1})	0,0814	0,0445	0,0425
ΔG^o (kJ.mol^{-1})	6,76	0,0445	0,0425
ΔH^o (kJ.mol^{-1})	-4,5091		
ΔS^o (kJ.mol^{-1}.K^{-1})	-0,0375		

Based on **Table 5,** the adsorption of Pb(II) ions by seaweed residue adsorbent takes place exothermally seen from the value of enthalpy change (ΔHo) which is negative and the value of entropy change (ΔSo) indicates the increasing system regularity of Pb(II) ions distribution during the adsorption process [20].

3.10 Desorption

In the desorption process, desorption was carried out using HNO$_3$ with several concentrations, namely 0.01 M, 0.1 M, and 0.5 M. **Table 6** shows that the best desorption process was obtained using 0.5 M HNO$_3$. This shows that high acid concentrations are better for the desorption of seaweed residue adsorbents.

Table 6. Adsorption and desorption process

HNO$_3$ (M)	% Adsorption	% Desorption
0,01	71,42	38,25
0,1	71,42	48,74
0,5	71,42	78,45

Desorption was carried out using a pH 3 solution, to confirm the previous conclusion that adsorption using a pH 5 solution is better than adsorption with a pH 3 solution, and the results showed that the adsorption process at pH 5 was much better than the adsorption process with pH 3.

3.11 Repeated Adsorption

In this desorption process, it was found that in the third to tenth adsorption process, %A had decreased to only 50%, but the adsorbent could still be used up to the tenth time, so this adsorbent is fairly efficient because it can be used repeatedly. In the desorption treatment of the adsorbent that had been used up to ten times, it was found that the amount that 0.5 M HNO3 could desorb in 5 minutes was 100.32, so in its use, it would be more effective if the adsorbent was used repeatedly, without being desorbed, because the preparation of the adsorbent is quite easy (only need to protonate the extraction residue) and the adsorbent desorption process can only release 100 ppm even though it has absorbed a lot of lead.
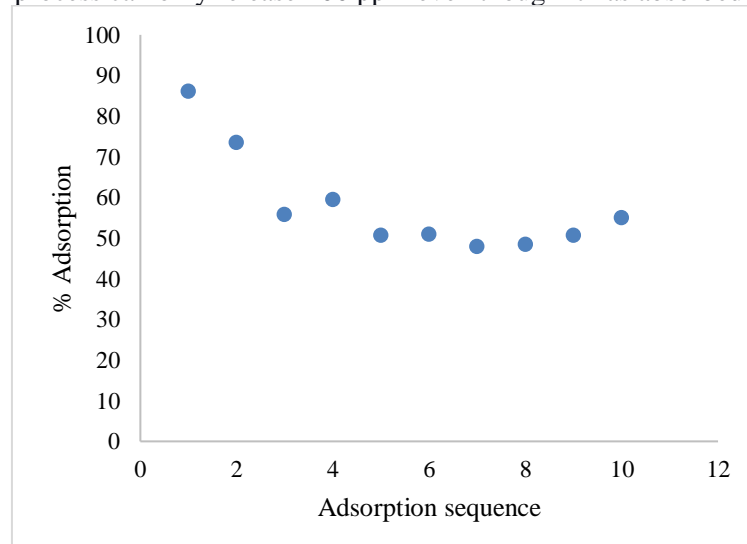
Figure 14. Repeated adsorption graph

4. Conclusion

The adsorbent was prepared by protonating the alginate extraction residue from *Sargassum sp.* seaweed using 0.1 M HCl for 6 hours. In determining the optimization of protonation, it was found that the optimum adsorption was obtained when the solution pH was 5, the adsorbent mass was 0.025 grams, the initial concentration of Pb(II) ions was 200 ppm and the contact time was 5 minutes. The adsorption process followed the Langmuir isotherm model with a maximum capacity of 416.67 mg.g^{-1}. The results of the kinetic study showed that the adsorption followed the pseudo-second-order reaction kinetics. The adsorption process of Pb (II) ions took place exothermically with a value of ΔH^o = -4.51 kJ.mol^{-1}, and a value of ΔS^o = -0.038 kJ.mol^{-1}.K^{-1}. The desorption process is better carried out using HNO$_3$ solution with a concentration of 0.5 M.

5. Acknowledgment

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